

## COUNTERCURRENT DISTRIBUTION OF HIGH-BOILING NEUTRAL OILS FROM A LOW-TEMPERATURE COAL TAR

Patricia A. Estep, Clarence Karr, Jr., William C. Warner,  
and Edward E. Childers

U. S. Department of the Interior, Bureau of Mines  
Morgantown Coal Research Center, Morgantown, W. Va.

### INTRODUCTION

In a comprehensive investigation of the composition of low-temperature bituminous coal tar it was necessary to analyze the high-boiling neutral oil fractions in the range 275° to 344° C. The method selected for this was fractionation by distillation, further separation by countercurrent distribution (CCD), and final analysis by infrared and ultraviolet spectrophotometry. A recent review on countercurrent distribution (10) shows that relatively little work has been done on the CCD of high-boiling neutral polynuclear compounds and nothing on separation of natural mixtures by this method. Golumbic (8) has reported an investigation of the partition coefficient of 18 polynuclear compounds in the solvent system cyclohexane/80 percent ethanol and proposed this solvent system for the analysis of the heavy-oil fractions of coal-hydrogenation products. Chang (5) reported on the partition coefficient of 24 aromatic compounds in  $\beta, \beta'$ -oxydipropionitrile/isooctane and proposed this solvent system for CCD separations of petroleum fractions and oils derived from coal tars. Mold (11) has recently conducted work on the CCD of polycyclic aromatic compounds with a solvent system containing tetramethyluric acid but did not analyze natural mixtures. The present work fully demonstrates the capabilities of CCD, supplemented by infrared and ultraviolet spectroscopy for the separation and analysis of complex high-boiling neutral aromatic coal tar, shale oil, or petroleum components. It was found that class separations were sufficient to allow reliable spectrophotometric analyses to be applied. Many specific isomers occurring in sufficiently large enough amounts were individually determined.

### EXPERIMENTAL

Preliminary Fractionation by Distillation. - The neutral oil used in this work was obtained from a low-temperature West Virginia bituminous coal tar. Previous reports (3,4) have presented the analysis of this material for fractions up to the present boiling range, using gas-liquid chromatography. In two separate distillations, the 29 neutral oil fractions analyzed in the present work were obtained, these representing 33.46 wt pct of the total neutral oil (the total neutral oil distilling up to about 360° C represents 16.92 wt pct of the tar). Complete data for the first of these distillations, including analysis of fractions 1 to 8, is included in a previous paper (3). The second distillation was made on a 47.2 g charge, giving 38.7 g distillate, 7.7 g residue, and 0.9 g loss and hold up. This material was distilled at 3.0 mm Hg with a reflux ratio of 20 to 1 in a spinning band still. Equivalent atmospheric boiling points were estimated from a standard nomograph. Infrared and ultraviolet spectra were obtained on all distillate fractions. These were combined on the basis of qualitative similarity to give 14 samples which were each fractionated by countercurrent distribution.

Countercurrent Distribution. - The instrument used was a Craig 60-tube all-glass model with an automatic fraction collector. The tube capacity for each phase was 40 ml. The instrument was operated to give 120 transfers and 60 tubes were collected in the fraction collector. Each distribution was made with a charge of 500 milligrams, obtained by using the proper volume of a solution of known concentration of the distillate fraction in the upper phase. The upper phase solvent was spectral grade isooctane, and the lower phase was a 90 wt pct ethanol in water mixture. This solvent system was chosen on the basis of its ability to separate various aromatic hydrocarbons from each other. A thorough investigation was conducted on anthracene, a typical component of these neutral oil fractions. Its partition coefficient in a variety of solvent pairs was determined, and the final choice was made for that in which the value was nearest 1. This placed the bulk of the material where enough tubes could be efficiently utilized in the separations. The solvent system choice was also limited to those mixtures sufficiently immiscible to give complete separation of layers during the preset instrument cycling time. The distributions were carried out at 26° C, and the solvents were pre-equilibrated at the same temperature. This pre-equilibration produced a volume change for equal volumes to 1.83 parts 90 wt pct ethanol per 1.00 parts isooctane after equilibration. The equilibrated solvents were used in making all necessary dilutions for ultraviolet analysis.

Spectrophotometric Analysis. - Ultraviolet spectra were obtained on the contents of all CCD tubes, taken directly from the instrument, on a Perkin-Elmer Model 350 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer equipped with a Perkin-Elmer 6x ultramicro sampling unit mounted in the sample beam. The sample holder, designed to mount the ultramicrocavity cells in this unit, has been described (6). Sample preparation preceding infrared analysis was as follows:

The contents of a single tube after ultraviolet analysis were placed in a 150-ml distillation flask and dry nitrogen passed slowly into the flask through a glass tube extending nearly to the bottom of the flask where the tube was drawn into a fine tip. The nitrogen flowed out through the side arm. When the solvent was completely removed, the material was transferred from this flask by means of a 6-in. hypodermic needle and syringe and several washings of carbon disulfide into a small tared tapered tube. The CS<sub>2</sub> was evaporated from this small tube with nitrogen through a syringe needle. It was seen from infrared spectra that the last traces of CS<sub>2</sub> could be removed by this method. The small amount of liquid material in the tip of this tube was first weighed and then transferred with the aid of a 50 µl microsyringe to an ultramicrocavity NaCl cell (purchased from the Barnes Engineering Company). Samples were run undiluted in these cells whenever possible. When there was not enough sample recovered to fill the cell cavity, the material was diluted with CS<sub>2</sub> and the infrared spectrum obtained in solution.

Determination of Distribution Curves. - The amount of material recovered in each tube was plotted to obtain a weight distribution for each run. The amount of material in a single tube typically ranged from 0.5 to 21 milligrams. Ultraviolet absorbance distribution curves also were prepared at various key wavelengths for each run. These were used for the determination of peak tubes of major components and in the quantitative analysis. When there was no peak tube discernible on the distribution plot for minor or trace components determined to

be present from spectra, it was possible to resolve the "envelope" of ultraviolet absorbance into its component parts. Since the countercurrent distributions are essentially Gaussian and symmetrical, it is possible to construct individual absorbance distribution curves by following the appearance and disappearance of individual bands in consecutive fractions and noting the peak tubes from spectra. This procedure was also helpful in determining which bands belonged to the same compound.

## RESULTS AND DISCUSSION

The results of the distillations are given in Table 1. On the basis of the qualitative information from ultraviolet and infrared spectra, the constituents from each CCD fractionation were distinguished and assigned numbers. It was essential to number these constituents since they frequently appeared in more than one run. A total of 51 separate identifications were made in this 69° C boiling range, and these are shown in Table 2.

The quantitative analyses for aromatics were conducted in the ultraviolet using absorptivities at characteristic bands where interferences from other constituents were at a minimum. Absorbance values were obtained from the curves already described. Where the ultraviolet absorption bands for components overlapped too greatly, their relative amounts could generally be estimated from their infrared bands. In those instances where very similar isomers overlapped extensively, they were analyzed as a class rather than as individual compounds. The qualitative and quantitative analyses of each class are described under separate headings.

From the quantitative data obtained for each constituent, plots of milligrams vs. tube number were prepared. Figures 1, 2, and 3 show these distribution curves for only 3 of the 14 neutral oil fractions. These are for CCD numbers 4, 9, and 14. Tubes are numbered from 0 to 59 in the direction of transfer in the instrument and from 0 up in the order of use in the fraction collector. The numbers on the distribution curves in Figures 1, 2, and 3 refer to some of the constituents listed in Table 2. The weight-percent of each constituent in the neutral oil was obtained from the distribution curves and the weights of the original distillate fractions. These quantitative results are summarized in Table 3.

o-Dimethylphthalate. - Identification of this compound was made by infrared spectroscopy. Its location in the lower tube numbers of the lower phase is in line with its polarity.

Carbazoles. - The weak but significant polar character of the unsubstituted nitrogen atom of carbazoles places this class in the lower numbered tubes of the lower phase, beginning with the parent structure in tube 27 of CCD No. 9. Subsequent runs show the peak tube to shift to tubes 29 and 31, indicating methylation, and both infrared and ultraviolet spectra confirmed the presence of monomethyl carbazoles. The quantitative determination of carbazole and its methyl derivatives was straightforward, using the absorption band at 230 to 240 mμ. For the determination of the mixed monomethyl isomers, the absorptivity data used was obtained from available samples of 1- and 2-methylcarbazole. Infrared literature spectra were available for the 3- and 4-methylcarbazoles (12), and ultraviolet was available for 3-methylcarbazole (9).

Long-chain Aliphatic Hydrocarbons. - These were effectively separated from aromatic hydrocarbons in the first 15 tubes of the fraction collector in each CCD run. Infrared analysis (7) showed this aliphatic material to consist of five classes:  $\alpha$ -olefins, branched  $\alpha$ -olefins, trans-internal olefins, n-alkanes, and 2-methylalkanes. Since the CCD solvent system was selected for optimum separation of aromatics, there was only a small separation by class for the aliphatic compounds. In Table 2 each class was assigned a single number throughout the entire boiling range although boiling points indicate a change in molecular weight from  $C_{15}$  through  $C_{20}$ .

Alkyl naphthenes. - According to Bellamy (2), the infrared bands observed at 10.72, 10.50, 10.27, and 9.73  $\mu$  in aliphatic fractions can be assigned to the ring deformation vibrations of six-membered ring naphthenes. An estimate of their concentration was made using data from literature spectra (1).

Aliphatic Carbonyl. - The carbonyl bands at 5.72 to 5.93  $\mu$  along with the  $CH_2$  rocking vibration at 13.88  $\mu$  were assigned to aliphatic carbonyl, either ketones or esters. The fairly long chain, as indicated by the intensity of the 13.88  $\mu$  band, balances the polar effect of the carbonyl group to place them in tubes 56 to 58 of the fraction collector. Estimates of concentration for this class were made by using absorptivity data for the carbonyl band from pure samples of aliphatic esters.

Naphthalenes. - Alkyl naphthalenes were identified in all neutral oil fractions. On the basis of boiling point and ultraviolet correlations, it was found that they were predominantly polymethylnaphthalenes. There was no evidence of any long chain or branched alkyl substitution. Infrared bands at 6.25 and 9.67  $\mu$  along with strong out-of-plane hydrogen deformation vibration bands in the 11.0 to 14.0  $\mu$  region were observed. The increasing number of possible isomers with increasing molecular weight of methylnaphthalenes made identification of specific isomers extremely difficult. It was observed from this laboratory's data and a collection of methylnaphthalene spectra from the literature, that in general, for polymethylnaphthalenes the specific absorptivity of the 230 m $\mu$  band decreases regularly in intensity with increasing molecular weight. The values for each carbon number were in a range narrow enough to justify the use of an average. The average specific absorptivity for 14 trimethylnaphthalenes ( $C_{13}$ ) was 530, for 7 tetramethylnaphthalenes ( $C_{14}$ ), 442, for 3 pentamethylnaphthalenes ( $C_{15}$ ), 346, and for 4 hexamethylnaphthalenes ( $C_{16}$ ), 317. An average specific absorptivity of 7 literature ethylmethylnaphthalenes ( $C_{13}$ ) falls very close to the value of trimethylnaphthalenes ( $C_{13}$ ), and an average of 4 diethylmethylnaphthalenes ( $C_{15}$ ) falls very close to that of pentamethylnaphthalenes ( $C_{15}$ ).

Hydroaromatics and Biphenyls. - A broad ultraviolet band at 259 m $\mu$  at a maximum in tubes 11 to 14 FC represented a mixture of biphenyls and hydroaromatics. Biphenyls were indicated by a series of shoulders occurring on this major band and also by an infrared band at 14.30  $\mu$ . The hydroaromatic structure was indicated by the aromatic band at 6.25  $\mu$  which, although present, was relatively weak. Additional evidence to support this class was obtained from ultraviolet quantitative data. From the actual weight of these fractions and the observed absorbances, ultraviolet absorptivities were approximated and found to be low, indicating saturation of aromatic rings.

**Fluorenes.** - Fluorenes were identified by their distinctly characteristic ultraviolet spectra and their strong out-of-plane hydrogen deformation bands in the infrared. The ultraviolet band at 300 m $\mu$ , which shifts to slightly higher wavelengths for methyl isomers, fortunately occurs in a region where analysis was unhindered by other components. For fluorene and 1-methylfluorene, analysis was straightforward, using specific absorptivity values of 59 and 41 respectively, determined at 300 m $\mu$  from available samples. The amount of the 2- and 3-methylfluorene mixture was determined at 260 m $\mu$  using an average specific absorptivity value of 116 obtained from pure samples.

**Phenanthrenes.** - Differentiation among the 1-methyl, 2-methyl, and 3-methyl isomers was readily made from strong infrared bands in the out-of-plane hydrogen deformation region at 11 to 14  $\mu$ . The strong ultraviolet band which ranged from 251 to 253.5 m $\mu$  in these CCD fractions indicated monomethyl-substituted phenanthrenes. This band shifts from 250.2 m $\mu$  for phenanthrene to a range of 251 to 254.4 m $\mu$  as observed in spectra of monomethylphenanthrenes. Dimethylphenanthrenes were also identified in the ultraviolet from the position of this strong band with a range of 252 to 256 m $\mu$ . From literature spectra of 12 dimethylphenanthrenes this range was observed to be 252 to 258 m $\mu$ . The shift in peak tubes accompanying the change in range of this ultraviolet band verified methylation. Phenanthrene determination was made in the ultraviolet, using a specific absorptivity value of 359 at 250.2 m $\mu$ . An average specific absorptivity of 322 was determined from pure samples of 1-methyl-, 2-methyl-, and 3-methylphenanthrene. Absorbances were read from the peak of the large band as it shifted from 251 to 253.5 m $\mu$ . The ratios of the individual monomethyl isomers were estimated from their strong infrared out-of-plane hydrogen deformation bands. For dimethylphenanthrenes, using the same intense ultraviolet band, an average specific absorptivity of 293 was determined from ultraviolet spectra of 12 dimethylphenanthrenes.

**Anthracenes.** - Qualitatively the distinction between anthracene and its monomethyl and dimethyl derivatives can best be made in the ultraviolet region where their longest wavelength bands are highly diagnostic. Neither the monomethyl nor the dimethyl anthracenes were substituted in the 9 or 10 position, as this causes a marked shift to longer wavelengths as compared to other positions. Quantitative analyses for anthracenes were conducted at 375.6 m $\mu$  for anthracene, 377.6 m $\mu$  for monomethylantracenes, and 380.0 m $\mu$  for dimethylantracenes. A specific absorptivity value of 43 for anthracene was determined from a pure sample. A monomethyl specific absorptivity value of 43 was obtained from a sample of 2-methylantracene and a literature spectrum of 1-methylantracene (15). From literature spectra of 7 dimethylantracenes, a value of 30 was determined for specific absorptivity.

**Dibenzofurans.** - Alkyldibenzofurans can be characterized in the infrared by a sharp, strong band in the 8.2 to 8.5  $\mu$  region (13) assigned to the C-O stretching vibration. The analysis was conducted in the ultraviolet region for dibenzofurans using a strong absorption band near 250 m $\mu$ . For dibenzofuran a value of 115 at 248.8 m $\mu$  for the specific absorptivity was obtained from a pure sample. The monomethyldibenzofurans were determined by using an average specific absorptivity value of 98 at 251 to 253 m $\mu$ , obtained from pure samples of 2-methyl-, 3-methyl-, and 4-methyldibenzofurans, and the spectrum for 1-methyldibenzofuran (14). For dimethyldibenzofurans, an average specific absorptivity value of 81 near 250 m $\mu$  was obtained from spectra of 6 dimethyldibenzofurans (14).

## REFERENCES

1. American Petroleum Institute Research Project 44. Catalog of Infrared Spectra. Carnegie Inst. Technol., Pittsburgh, Pa.
2. Bellamy, L. J. The Infra-red Spectra of Complex Molecules. John Wiley & Sons, Inc., New York, 1960, 2d ed., 425 pp.
3. Chang, Ta-Chuang Lo, and Clarence Karr, Jr. Gas-Liquid Chromatographic Analysis of Aromatic Hydrocarbons Boiling Between 202° and 280° in a Low-Temperature Coal Tar. Anal. Chim. Acta, v. 24, No. 4, April 1961, pp. 343-356.
4. \_\_\_\_\_. Gas-Liquid Chromatographic Analysis of Aromatic Hydrocarbons Boiling Up to 218° in a Low-Temperature Coal Tar. Anal. Chim. Acta, v. 21, No. 5, November 1959, pp. 474-490.
5. Chang, Yi-Chung, and Robert D. Wotring. Countercurrent Distribution of Some Aromatic Hydrocarbons. Anal. Chem., v. 31, No. 9, September 1959, pp. 1501-1504.
6. Estep, Patricia A., and Clarence Karr, Jr. A Liquid Ultramicrocavity Cell Holder for Use With an Infrared Beam Condenser. Appl. Spectry., v. 16, No. 5, October 1962, pp. 167-168.
7. \_\_\_\_\_. Quantitative Infrared Microanalysis of High-Boiling Aliphatic Neutral Oil Fractions. Anal. Chem., v. 36, No. 11, October 1964, pp. 2215-2218.
8. Golumbic, Calvin. Separation and Analysis of Polynuclear Compounds by Countercurrent Distribution. Anal. Chem., v. 22, No. 4, April 1950, pp. 579-582.
9. Haines, R. E. Bureau of Mines, Laramie Petrol. Res. Center, Laramie, Wyo., private communication, 1962.
10. Lederer, Michael, editor. Chromatographic Reviews. Elsevier Publishing Co., New York, v. 5 (covering the year 1962), 1963, 244 pp.
11. Mold, James D., Thomas B. Walker, and Lee G. Veasey. Selective Separation of Polycyclic Aromatic Compounds by Countercurrent Distribution With a Solvent System Containing Tetramethyluric Acid. Anal. Chem., v. 35, No. 13, December 1963, pp. 2071-2074.
12. Richards, R. E. Infra-red Spectrum and Structural Diagnosis: Substituted Carbazoles. J. Chem. Soc., 1947, pp. 978-979.
13. Trippett, S. The Synthesis of Methyl- and Dimethyl-dibenzofurans. J. Chem. Soc., January 1957, pp. 419-421.
14. \_\_\_\_\_. The University, Leeds, England, private communication, November 1959.
15. Wolthuis, Enno. Synthesis of Some Methyl-Substituted Anthracenes. J. Org. Chem., v. 26, No. 7, July 1961, pp. 2215-2220.

## ACKNOWLEDGMENTS

The authors wish to express their appreciation to: Chester Muth, Chemistry Department, West Virginia University, Morgantown, W. Va., for a sample of 4-methyldibenzofuran; A. Ladam, Centre d'Etudes et de Recherches des Charbonnages de France, for samples of 1-, 2-, and 3-methylfluorene and 2- and 3-methyldibenzofuran; S. Trippett, University of Leeds, England, for spectra of a variety of alkyl dibenzofurans; and W. E. Haines, Laramie Petroleum Research Center, Bureau of Mines, Laramie, Wyo., for a sample of 1-methylcarbazole and an ultraviolet spectrum of 3-methylcarbazole.

TABLE 1. - Fractional distillation of neutral oils

CCD No.	Distillate fraction No.	Boiling range, ° C		Weight, grams
		10 mm	760 mm	
1	9	138 - 139	275 - 276	9.0
	10	139 - 141	276 - 278	9.0
2	11	141 - 143	278 - 280	8.6
	12	143 - 144	280 - 282	9.4
3	13	144 - 146	282 - 284	9.2
	14	146 - 148	284 - 286	9.3
4	15	148 - 149	286 - 287	9.6
	16	149	287	3.6
				<sup>1</sup> 67.7
		3.0 mm	760 mm	
5	1	123 - 125	287 - 290	1.9
	2	125 - 127	290 - 292	2.0
6	3	127 - 128	292 - 293	1.6
	4	128	293	1.7
7	5	128 - 132	293 - 298	1.7
	6	132 - 134	298 - 300	1.9
8	7	134 - 135	300 - 301	1.6
	8	135 - 136	301 - 302	1.9
	9	136 - 137	302 - 303	1.6
9	10	137 - 138	303 - 305	1.9
	11	138 - 143	305 - 310	2.0
10	12	143 - 144	310 - 311	2.1
	13	144 - 145	311 - 313	2.0
11	14	145 - 148	313 - 316	2.2
	15	148 - 150	316 - 318	2.3
	16	150 - 152	318 - 321	2.0
12	17	152 - 153	321 - 322	2.0
	18	153 - 160	322 - 329	1.9
13	19	160 - 167	329 - 337	1.9
14	20	167 - 171	337 - 342	2.0
	21	171 - 173	342 - 344	.5
				<sup>2</sup> 38.7

<sup>1</sup> Fractions 9 through 16 are 9.72 weight-percent of the total neutral oil.

<sup>2</sup> An aliquot representing 23.74 weight-percent of the total neutral oil.

TABLE 2. - Countercurrent distribution of high-boiling neutral oils

Constituent Identity		Peak tube no.
No.		
<u>CCD NO. 1</u>		
1	Unknown I	34
2	Aliphatic carbonyl	58 FC
3	Dibenzofuran	44 FC
4	Acenaphthene	34 FC
5	Trimethylnaphthalenes (N <sub>1</sub> , N <sub>2</sub> , N <sub>3</sub> , N <sub>4</sub> )	26 FC
6	Hydroaromatics, Biphenyls	14 FC
7	Alkylnaphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	10.5 FC
9	Terminal olefin	10.5 FC
10	n-Alkane	9.0 FC
11	Branched-terminal olefin	8.5 FC
12	2-Methylalkane	6 FC
<u>CCD NO. 2</u>		
1	Unknown I	34.5
2	Aliphatic carbonyl	58 FC
3	Dibenzofuran	48 FC
13	Fluorene	44 FC
5	Trimethylnaphthalenes (N <sub>1</sub> , N <sub>2</sub> , N <sub>3</sub> , N <sub>4</sub> )	25 FC
14	Tri- or tetramethylnaphthalenes (N <sub>5</sub> , N <sub>6</sub> , N <sub>7</sub> )	25 FC
6	Hydroaromatics, Biphenyls	14 FC
7	Alkylnaphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	9 FC
9	Terminal olefin	9 FC
10	n-Alkane	8 FC
11	Branched terminal olefin	6 FC
12	2-Methylalkane	3.5 FC
<u>CCD NO. 3</u>		
15	o-Dimethylphthalate	4
1	Unknown I	33.5
2	Aliphatic carbonyl	58 FC
16	4-Methyldibenzofuran	48 FC
13	Fluorene	42 FC
14	Tri- or tetramethylnaphthalenes (N <sub>5</sub> , N <sub>6</sub> , N <sub>7</sub> )	26 FC

See footnotes at end of table.

Constituent		Peak
No.	Identity	tube no.
6	Hydroaromatics, Biphenyls	14 FC
7	Alkyl-naphthenes (6-membered ring)	10 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8.5 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	8 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 4</u>		
15	o-Dimethylphthalate	4
1	Unknown I	34
2	Aliphatic carbonyl	56 FC
16	4-Methyldibenzofuran	45 FC
13	Fluorene	42 FC
14	Tri- or tetramethylnaphthalenes (N <sub>5</sub> , N <sub>6</sub> , N <sub>7</sub> )	26 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	7.5 FC
11	Branched terminal olefin	7 FC
12	2-Methylalkane	3 FC
<u>CCD NO. 5</u>		
17	Unknown II	34.5
2	Aliphatic carbonyl	56 FC
18	2-Methyldibenzofuran	<sup>2</sup> 36 FC
19	3-Methyldibenzofuran	<sup>2</sup> 36 FC
16	4-Methyldibenzofuran	<sup>2</sup> 36 FC
20	1-Methyldibenzofuran	<sup>2</sup> 36 FC
21	Tetramethylnaphthalenes	23 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7.5, 12 FC
12	2-Methylalkane	5 FC

See footnotes at end of table.

Constituent		Peak
No.	Identity	tube no.
<u>CCD NO. 6</u>		
17	Unknown II	36
18	2-Methyldibenzofuran	<sup>2</sup> 36 FC
19	3-Methyldibenzofuran	<sup>2</sup> 36 FC
16	4-Methyldibenzofuran	<sup>2</sup> 36 FC
20	1-Methyldibenzofuran	<sup>2</sup> 36 FC
21	Tetramethylnaphthalenes	24 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8.5 FC
9	Terminal olefin	8.5 FC
10	n-Alkane	8.5 FC
11	Branched-terminal olefin	7.5 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 7</u>		
17	Unknown II	35
22	Aliphatic carbonyl	55 FC
23	Unknown III	55 FC
24	Dimethyldibenzofuran	<sup>2</sup> 41 FC
18	2-Methyldibenzofuran	<sup>2</sup> 41 FC
19	3-Methyldibenzofuran	<sup>2</sup> 41 FC
20	1-Methyldibenzofuran	<sup>2</sup> 41 FC
25	1-Methylfluorene	38 FC
26	2- and/or 3-Methylfluorene	38 FC
27	Dimethyldibenzofurans	24 FC
21	Tetramethylnaphthalenes	23.5 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 8</u>		
17	Unknown II	35
28	Unknown IV	55 FC
29	Phenanthrene	51 FC
30	Unknown V	48 FC
18	2-Methyldibenzofuran	<sup>2</sup> 44 FC
19	3-Methyldibenzofuran	<sup>2</sup> 44 FC
25	1-Methylfluorene	38 FC
26	2- and/or 3-Methylfluorene	38 FC

See footnotes at end of table.

Constituent		Peak
No.	Identity	tube no.
31	2, 4-Dimethyldibenzofuran	31 FC
27	Dimethyldibenzofurans	24 FC
32	Alkyl naphthalenes (N <sub>8</sub> , N <sub>9</sub> )	22.5 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	8 FC
9	Terminal olefin	8 FC
10	n-Alkane	8 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	5 FC
<u>CCD NO. 9</u>		
33	Carbazole	27
34	Unknown VI	37.5
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	48 FC
26	2- and/or 3-Methylfluorene	38 FC
31	Dimethyldibenzofuran (principally 2, 4-dimethyldibenzofuran)	30 FC
32	Alkyl naphthalenes (N <sub>8</sub> , N <sub>9</sub> )	22 FC
6	Hydroaromatics, Biphenyls	14 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 10</u>		
33	Carbazole	27
34	Unknown VI	38
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	47 FC
36	Carbonyl compound	42 FC
31	Dimethyldibenzofurans (principally 2, 4-dimethyldibenzofuran)	32.5 FC
32	Alkyl naphthalenes (N <sub>8</sub> , N <sub>9</sub> )	22 FC
6	Hydroaromatics, Biphenyls	13 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7, 10 FC
12	2-Methylalkane	4 FC

Constituent		Peak
No.	Identity	tube no.
<u>CCD NO. 11</u>		
33	Carbazole	27
34	Unknown VI	39
37	Unknown VII	54 FC
29	Phenanthrene	51 FC
30	Unknown V	48 FC
35	Anthracene	45 FC
38	2-Methylphenanthrene	43 FC
39	3-Methylphenanthrene	41 FC
40	1-Methylphenanthrene	38 FC
41	Dimethyldibenzofurans	30 FC
42	Alkylnaphthalenes (N <sub>11</sub> , N <sub>10</sub> )	21 FC
6	Hydroaromatics, Biphenyls	13 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	7, 10 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 12</u>		
43	1-Methylcarbazole	<sup>2</sup> 26.5
33	Carbazole	<sup>2</sup> 26.5
44	Unknown VIII	42
35	Anthracene	45 FC
38	2-Methylphenanthrene	<sup>2</sup> 40 FC
39	3-Methylphenanthrene	<sup>2</sup> 40 FC
40	1-Methylphenanthrene	<sup>2</sup> 40 FC
45	1- and/or 2-Methylantracene	40 FC
41	Dimethyldibenzofurans	28 FC
42	Alkylnaphthalenes (N <sub>11</sub> , N <sub>10</sub> )	18.5 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	6, 9.5 FC
9	Terminal olefin	6 FC
10	n-Alkane	7 FC
11	Branched-terminal olefin	6, 9 FC
12	2-Methylalkane	4.5 FC
<u>CCD NO. 13</u>		
46	2- and/or 3-Methylcarbazole	<sup>2</sup> 29
43	1- and/or 4-Methylcarbazole	<sup>2</sup> 29
47	Unknown IX	46
38	2-Methylphenanthrene	<sup>2</sup> 40 FC

See footnotes at end of table.

Constituent		Peak
No.	Identity	tube no.
39	3-Methylphenanthrene	<sup>2</sup> 40 FC
40	1-Methylphenanthrene	<sup>2</sup> 40 FC
45	1- and/or 2-Methylanthracene	38 FC
48	Alkyldibenzofurans	26 FC
42	Alkyl-naphthalenes (N <sub>11</sub> , N <sub>10</sub> )	18.5 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	7 FC
9	Terminal olefin	7 FC
10	n-Alkane	6 FC
11	Branched-terminal olefin	7 FC
12	2-Methylalkane	4 FC
<u>CCD NO. 14</u>		
46	2- and/or 3-Methylcarbazole	<sup>2</sup> 31
43	1- and/or 4-Methylcarbazole	<sup>2</sup> 31
47	Unknown IX	46
49	Unknown X	57 FC
45	1- and/or 2-Methylanthracene	39 FC
50	Dimethylphenanthrenes	35.5 FC
51	Dimethylanthracenes	32 FC
48	Alkyldibenzofurans	25 FC
42	Alkyl-naphthalenes (N <sub>11</sub> , N <sub>10</sub> )	18 FC
6	Hydroaromatics, Biphenyls	11 FC
8	trans-Internal olefin	6 FC
9	Terminal olefin	6 FC
10	n-Alkane	6 FC
11	Branched-terminal olefin	6 FC
12	2-Methylalkane	3 FC

<sup>1</sup> FC = fraction collector.

<sup>2</sup> Peak tube for a mixture of compounds.

TABLE 3. - Quantitative analysis of neutral oils  
boiling from 275° to 344° C

Constituent	Weight-percent in neutral oil <sup>1</sup>
Alkylbinuclear naphthenes	0.15
n-Alkanes	3.16
2-Methylalkanes	1.09
Terminal olefins	2.42
Branched-terminal olefins	.37
trans-Internal olefins	1.29
Aliphatic carbonyl	.21
	<u>8.69</u>
Acenaphthene	.37
Hydroaromatics, biphenyls	3.02
Trimethylnaphthalene, No. 5	1.88
Alkyl-naphthalenes (tetramethyl), No. 14	2.60
Alkyl-naphthalenes, Nos. 21, 32, 42	7.75
	<u>12.23</u>
Fluorene	.20
1-Methylfluorene	.10
2- and/or 3-Methylfluorene	.23
	<u>.53</u>
Phenanthrene	.39
1-Methylphenanthrene	.11
2-Methylphenanthrene	.19
3-Methylphenanthrene	.23
Dimethylphenanthrenes	.23
	<u>1.15</u>
Anthracene	.05
Monomethylantracenes	.04
Dimethylantracenes	.01
	<u>.10</u>

<sup>1</sup> Total neutral oil (distilling up to about 360° C) constituted 16.92 weight-percent of the total tar.

(Continuing)  
TABLE 3. - Quantitative analysis of neutral oils  
boiling from 275° to 344° C

Constituent	Weight-percent in neutral oil <sup>1</sup>
Dibenzofuran	0.32
1-Methyldibenzofuran	.19
2-Methyldibenzofuran	.27
3-Methyldibenzofuran	.46
4-Methyldibenzofuran	.34
Dimethyldibenzofurans	3.84
(Approximately 50 percent 2, 4-dimethyldibenzofuran)	
Alkylated dibenzofurans (trimethyl-)	.68
	<hr/> 6.10
o-Dimethylphthalate	.03
Carbazole	.09
1- and/or 4-Methylcarbazole	.08
2- and/or 3-Methylcarbazole	<hr/> .17
Unknowns I through X	1.02

<sup>1</sup> Total neutral oil (distilling up to about 360° C) constituted 16.92 weight-percent of the total tar.

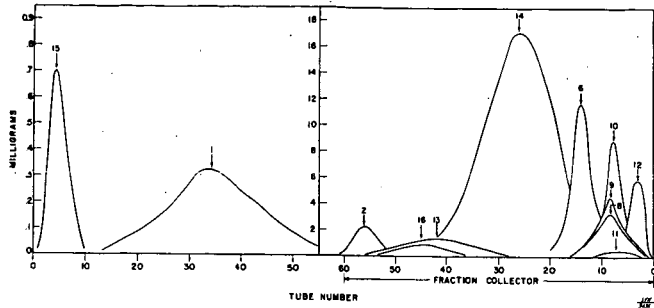


FIGURE 1. - Countercurrent Distribution of Neutral Oil, Run No. 4.

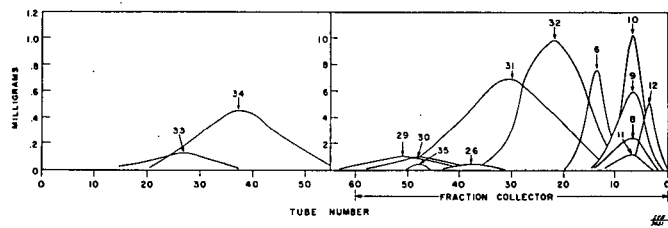


FIGURE 2. - Countercurrent Distribution of Neutral Oil, Run No. 9.

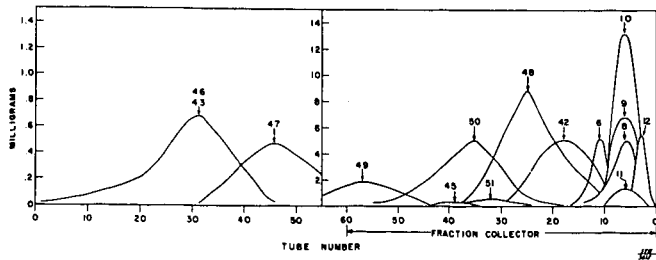


FIGURE 3. - Countercurrent Distribution of Neutral Oil, Run No. 14.